Peroxide bleaching with zeolites Part 2: Bleaching of pine TMP and eucalypt CCS

DANIEL FINNEGAN*, KAREN STACK† AND LAWRIE DUNN‡

A combination of zeolite and sodium citrate was found to be an effective alternative to DTPA addition in alkaline peroxide bleaching of pine TMP in the presence of manganese ions, but not in the bleaching of Eucalypt CCS pulp. The addition of the zeolite had no effect on strength properties of the TMP and CCS pulps. Some small improvements in optical properties were observed.

The type of zeolite used was important. Addition of small amounts of sodium citrate to the zeolite system improved the zeolite's ability to chelate metal ions from the pine TMP fibre. Sodium citrate appears to act as a transfer agent, facilitating the migration of metal ions from the pulp fibres to the zeolite.

In the presence of manganese, the alkaline conditions of the Eucalypt CCS resulted in the formation of oxidized manganese species that actively decompose peroxide. Zeolite and citrate appear to be unable to complex these metal species. DTPA, on the other hand, is effective in complexing the Mn-O species present in CCS.

Keywords

Alternative chelating agents, manganese ions, mechanical pulping, peroxide bleaching, sodium citrate, zeolites

ONE of the main limiting factors in peroxide bleaching of mechanical wood pulps is the decomposition of peroxide by metal ions such as copper, iron and manganese (*1–6*). DTPA is added as a chelating agent to complex metal ions and minimize their effect on bleaching processes. There is some concern over the possible environmental impact of DTPA in effluent from bleach plants. Several replacement chemicals for DTPA have been proposed (*7*), two of which are zeolite and sodium citrate.

In a previous paper (*8*), the effects of zeolites on manganese induced peroxide decomposition in the absence of pulp was investigated. Zeolite with sodium citrate was found to reduce decomposition under certain conditions. The zeolite-citrate system prevented decomposition only if the chelating agent was added before alkaline addition. For commercially available zeolites examined zeolite-A performed better as a chelating agent than types X and Y due to a greater exchange capacity based on the Si:Al ratio. Addition of small amounts of citrate to the zeolite reduce the rate of decomposition compared to a system containing zeolite alone. Increasing the reaction temperature reduced the efficiency of the zeolite-A and citrate system.

The aim of this paper is to investigate the effect of addition of zeolites and citrate on peroxide decomposition in the peroxide bleaching of pine thermomechanical pulp (TMP) and eucalypt cold caustic soda pulp (CCS). Manganese has been added to the pulps to induce peroxide decomposition. The effects on strength and other optical properties are also reported.

EXPERIMENTAL

Materials

Radiata pine TMP (brightness 60.9% ISO) and eucalypt CCS (brightness 46.2% ISO) were obtained from Fletcher Challenge Paper, Boyer Tasmania. The pulps were dewatered to approximately 20% concentration (p.c.) and crumbed before storage in a freezer at -9°C until use. All chemicals were analytical grade quality, except for laboratory grade potassium iodide, a commercial sample of sodium diethylenetriaminepentaacetic acid (Na_5DTPA) and MilliQ high purity water. The three sodium zeolites were obtained from various commercial suppliers: zeolite-A from Albemarle Corporation (USA), zeolite-X from PQ Zeolites (Netherlands) and zeolite-Y from Linde Division of Union Carbide (USA). Acid zeolites were prepared from the sodium zeolite by stirring in ammonium nitrate for 24 hours and drying in a muffle furnace at 400°C.

Bleaching

Treatment of pulp with chelating agent: Into a 20 L stainless steel mixing bowl were placed ≈ 1000 g o.d. defrosted pulp, 10 L of deionized water and 2% DTPA on o.d. pulp. The contents were mixed for 1 hour. The pulp slurry was placed in a pneumatic pulp dewatering press to remove as much liquid as possible. A further 10 L of deionized water was added onto the pulp cake in the press. The surface water was removed by vacuum before further pressing. The pulp was crumbed and stored in a freezer at -9°C until use.

Bleaching with hydrogen peroxide: The TM and CCS pulps were bleached at 5% p.c. in 500 mL polyethylene bottles with a reaction volume of 400 mL. Manganese (as manganese sulfate in deionized water) was added to 20 g o.d. pulp and mixed in a waterbath at 70°C for 5 minutes. The amount of manganese added was 135 mg/L (on pulp) for TMP and 40 mg/L for CCS. The appropriate chelating agent was added and stirred for a further minute before addition of sodium hydroxide (2.5% *m/m* on pulp) and hydrogen peroxide (2% *m/m* on pulp). The mixture was then stirred for 3 hours at 70°C. After bleaching, a sufficient amount of pulp to make three brightness sheets was removed. The pH of this pulp was adjusted to pH 4.5 with 10% sulfuric acid solution before the brightness sheets were made. The handsheets were allowed to dry overnight before brightness testing with a Datacolor Elrepho 2000. Residual peroxide measurements were made on the remaining pulp slurry.

Determination of residual peroxide: Part of the bleached pulp slurry was filtered for residual peroxide determination. A 10 mL sample was pipetted into a 250 mL conical flask containing 10 mL of 10% *m/m* sulfuric acid, 1 drop of 10% *m/m* ammonium molybdate and 50 mL of distilled water. Potassium iodide (2.0 g) was added to the flask, swirled and the contents titrated against standardized ≈ 0.01 M sodium thiosulfate (*9*). The residual peroxide was then calculated from the formula:

$$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

* M.Sc Research Student, Member Appita?
† Associate Lecturer, Member Appita
‡ Senior Lecturer, Member Appita
Department of Chemistry, University of Tasmania, GPO Box 252C, Hobart, Tas. 7001.

Physical testing of handsheets

Bleaching of pulp prior to handsheet making: Untreated and dewatered pine TM pulps were bleached using hydrogen peroxide in the manner previously described with the exception of no manganese and alkali charge of 1.75%.

Chelated eucalypt CCS was bleached using hydrogen peroxide in the manner previously described with the exception of 10 mg/L manganese and alkali charge of 1.75%. The 10 mg/L manganese was added to account for any metals lost during chelation, as the eucalypt CCS could not be obtained from the Boyer mill without some addition of DTPA.

Handsheet making and physical testing: Handsheets were made after the pulp was adjusted to pH 4.5. The handsheets were made in accordance with AS/NZS 1301.203s: 1993, using equipment in accordance with AS/NZS 1301.214s:1993. The handsheets were tested in accordance with AS/NZS 1301.208s:1997. The handsheets were also tested for optical properties using AS/NZS 1301.454s:1992.

RESULTS AND DISCUSSION

Bleaching of pine TMP with hydrogen peroxide

Figure 1 shows the effect of zeolite-A with and without citrate and sodium citrate addition with 2% H_2O_2 and 2.5% NaOH on ISO brightness of pine TMP and residual peroxide. Metal ions present in the pulp samples were removed by chelation prior to the experiments. 135 mg/L manganese was then added to induce peroxide decomposition. In the absence of the addition of a chelating agent these conditions (2% H_2O_2, 2.5% NaOH, 135 mg/L Mn^{2+}) resulted in rapid peroxide decomposition and decreased brightness and no residual peroxide. A decrease of 6% ISO brightness from the initial pulp brightness occurred due to alkali darkening.

The results in Figure 1 indicate that addition of zeolite-A has a beneficial effect on brightness and residual peroxide concentration in peroxide bleaching of pine TMP in the presence of manganese ions. Addition of sodium citrate (0.5%) further improved pulp brightness and residual peroxide. The zeolite charge required to reach the pulp brightness prior to alkali addition (60.9% ISO) was only 2% for the system containing zeolite-A and citrate compared to 5% for zeolite-A alone. Furthermore, on the basis of brightness results, a charge of 5% zeolite-A and 0.5% citrate is comparable to 10% zeolite-A in the system without citrate, which represents a saving of about half the chemical charge. The maximum brightness for the system occurred at a charge of 7.5% zeolite-A and 0.5% citrate. The addition of citrate to zeolite-A not only improved brightness, but also significantly improved the residual peroxide with residuals increasing up to a charge of 7.5% zeolite-A and 0.5% citrate. Benefits in chemical charge were also observed for the residual peroxide as the residual peroxide concentration for 2% zeolite-A and 0.5% citrate was higher than the system containing up to 10% zeolite-A alone. These results are opposite to those in the absence of pulp (*8*), where increasing the zeolite-A charge increased the rate of peroxide decomposition. One possible explanation for this difference is that more zeolite is needed to compete with lignin and cellulose for the metal ions and so reducing metal catalysed peroxide decomposition. Furthermore, peroxide can react with the pulp fibres which might lower the overall ratio of peroxide to zeolite and hence lower decomposition due to peroxide-zeolite interactions.

The effect of sodium citrate addition on peroxide bleaching of pine TMP is shown in Figure 2. In the absence of zeolite, the addition of sodium citrate to the pulp and bleaching reagents increased the brightness from 55% ISO. An addition of 2% citrate was needed to increase the pulp brightness to the value of 60.9% prior to the alkali addition. At this point, the first significant residual peroxide concentration also occurred. Addition of zeolite-A to the system dramatically improved residual peroxide and brightness response of the bleaching stage. With the addition of 5% Zeolite-A and no citrate, a brightness level of 61% was achieved. This is significantly higher than the brightness achieved in the absence of zeolite due to the chelating effect of zeolite-A. A maximium in brightness occurred after the addition of 0.5% citrate in the presence of 5% zeolite-A (Fig. 2) and the brightness remained constant as the addition of citrate increased. In contrast, Figure 1 shows that addition of citrate to the zeolite system caused constant improvement in brightness

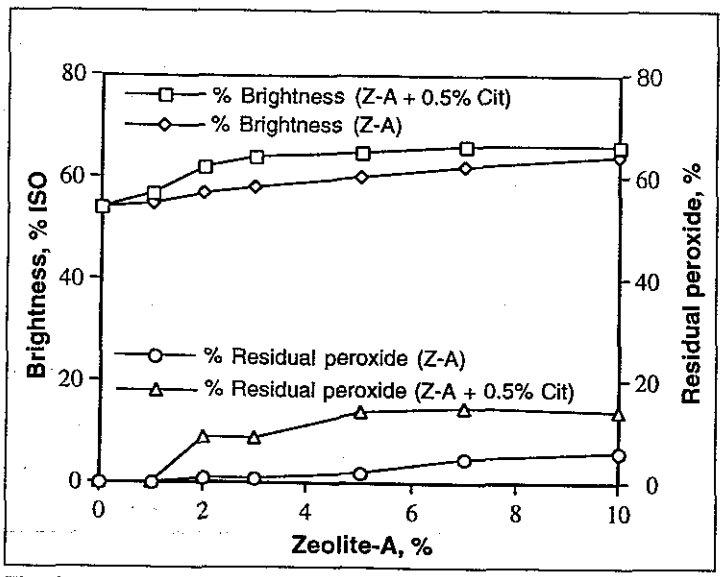

Fig. 1 The effect on brightness and residual concentration of peroxide bleached pine TMP by zeolite-A concentration with and without citrate.

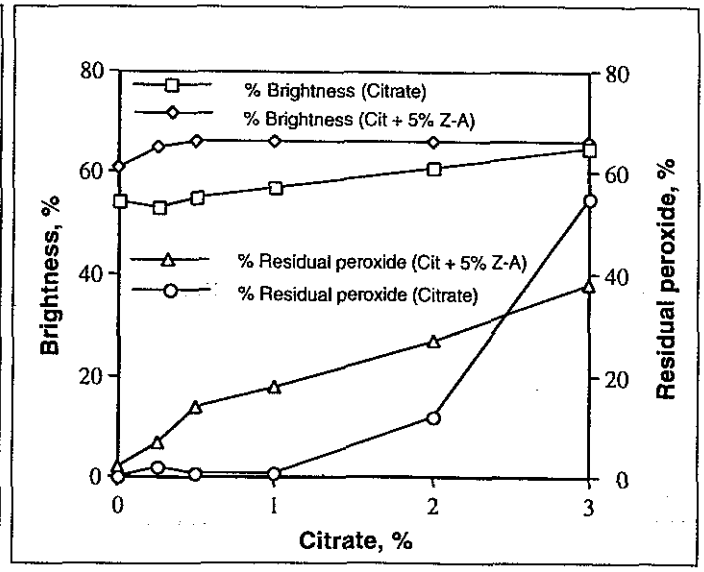

Fig. 2 The effect on brightness and residual peroxide concentration of peroxide bleached pine TMP by sodium citrate.

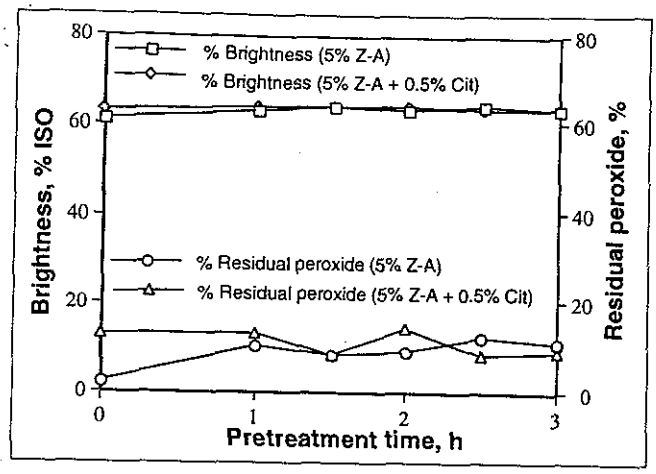

Fig. 3 The effect on brightness and residual peroxide concentration of peroxide bleached pine TMP by pretreatment time with zeolite-A.

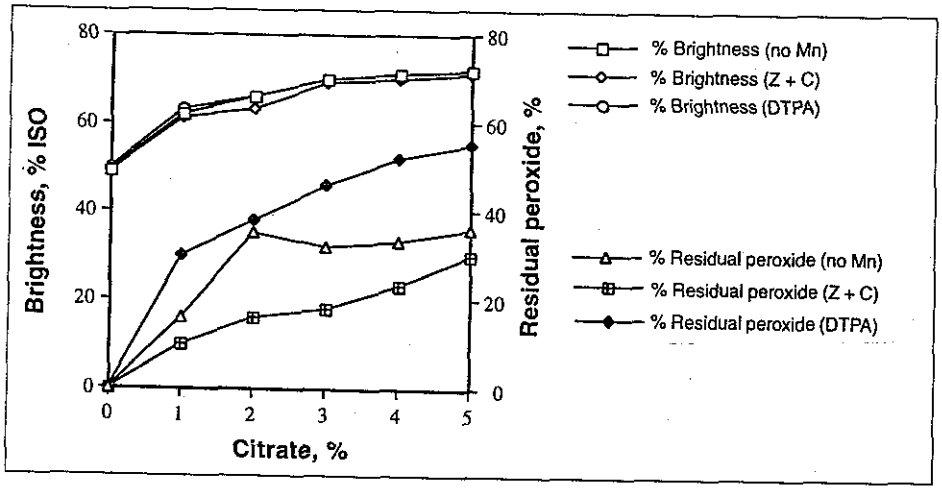

Fig. 4 The effect on brightness and residual peroxide concentration of chelated bleached pine TMP by peroxide.

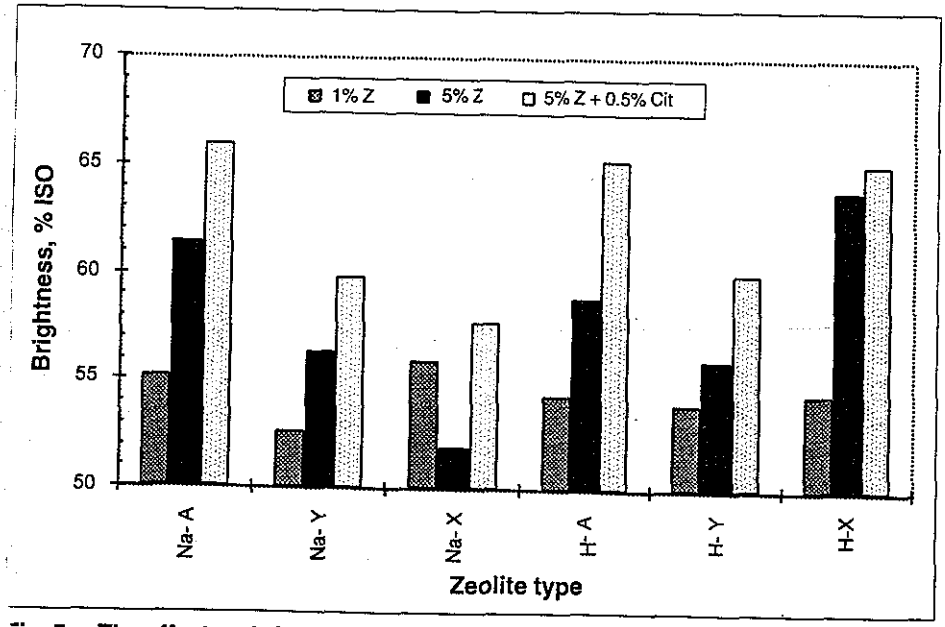

Fig. 5 The effect on brightness of peroxide bleached pine TMP by zeolite type.

over that of zeolite alone until maximum brightness was obtained, under the conditions employed in this study. However it should be noted that in Figure 2 the brightness results at or above 0.5% citrate addition with 5% zeolite-A are equivalent to the maximum brightness obtained in Figure 1. Furthermore while no additional brightness gains occurred with addition of citrate above 0.5% with 5% zeolite-A, the residual peroxide increased suggesting that the additional citrate helped to prevent manganese induced decomposition. Therefore it is most likely that the upper brightness obtained is 'pulp limited' due to bleaching pulp concentration and pulp chemistry, rather than a lack of peroxide (*10*).

The effect of pretreatment time on the performance of zeolite based chelation of pine TMP is shown in Figure 3. With these results there was no washing stage between the pretreatment and the bleaching stage. Bleaching chemicals were added directly to the pulp containing chelating agents. Optimum pretreatment time occurred within an hour for both zeolite and zeolite-citrate systems in terms of brightness and residual peroxide.

Figure 4 shows the effect of peroxide charge on bleaching. Brightness and residual peroxide concentrations both increased with increased peroxide charge. These results also show that the combined zeolite-citrate system performed nearly as well as DTPA for brightness over the whole range of peroxide charges. DTPA addition resulted in higher residual peroxide concentrations compared to the zeolite-citrate system. On that basis, DTPA would be a better choice if white water is recycled in a closed bleach plant.

The effect of zeolite type under various conditions on peroxide bleaching of pine TMP is illustrated in Figures 5 and 6. These results show that residual peroxide (Fig. 6) and brightness (Fig. 5) increased with zeolite charge, particularly when citrate is added to all of the zeolite types with exception of sodium zeolite-X. The acid form of zeolite-X performs better than the sodium form in brightness and residual peroxide. This effect might be related to pH, with acid from the zeolite-X possibly neutralizing some of the alkali, thus reducing metal catalysed decomposition and alkali darkening rather than an improved chelating ability. This conclusion is supported by the results in the absence of pulp (*8*), where zeolites-X and -Y showed significantly poorer uptake of manganese compared to zeolite-A based on the more

rapid peroxide decomposition curves.

These results for acid zeolite-X may also be explained by the absence of sodium ions which on hydrolysis can change the surface exchange sites. The site chemistry is changed from Al-O⁻ Na⁺ to the less preferred Al-O-H with sodium ions present in the liquid phase. The sodium ions prevent the migration of hydrogen ions into the liquid phase by electric field effects. The acid zeolite does not have sodium ions present so the chemistry of the site can revert to Al-O⁻ for optimum cation exchange. Zeolite-Y which has the same pore structure is not affected in the same manner as zeolite-X because it does not have as many exchange sites. Zeolite-A is also not affected in the same way as zeolite-X because it does not have a free liquid phase due to its small pore size. Furthermore most of the exchange sites for zeolite-A are located inside the ring structures rather than on surfaces facing voids and pores (*11*).

Figure 5 also confirms that zeolite-A is the best of the three commercial zeolites for use in peroxide bleaching.

Bleaching of eucalypt CCS with hydrogen peroxide

The effect of zeolite-A and/or sodium citrate on peroxide bleaching of eucalypt CCS and the corresponding residual peroxide concentrations using the bleaching conditions described in the experimental method are shown in Figure 7. Zeolite-A addition has no effect in preventing manganese induced peroxide decomposition in the bleaching of eucalypt CCS and also in the absence of peroxide bleaching, zeolite-A addition only has a small effect on pulp brightness (<2% ISO) despite a reasonably large dose rate (10%) of zeolite-A. This small increase corresponds to the contribution of

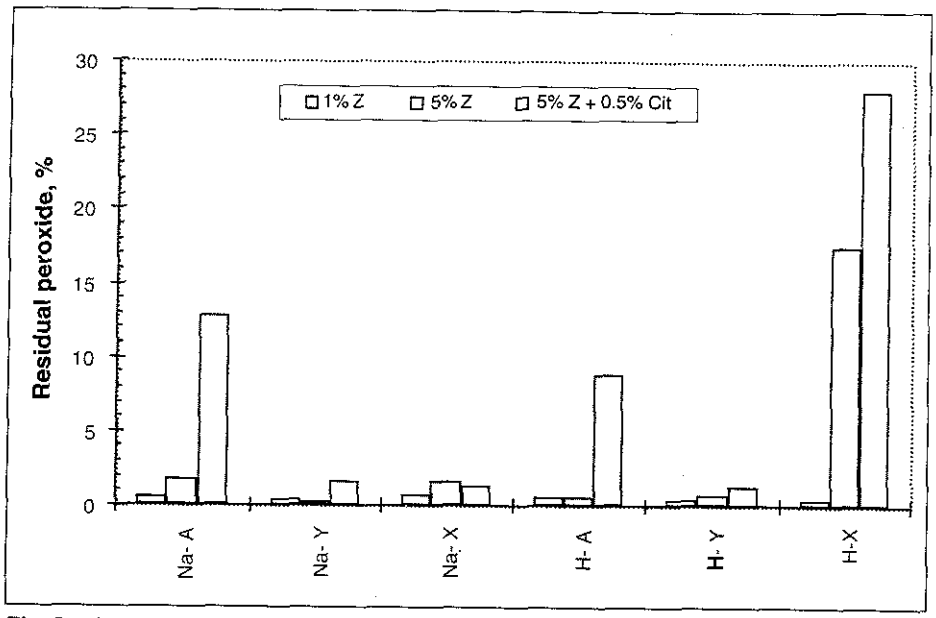

Fig. 6 **The effect of residual peroxide concentration of peroxide bleached pine TMP by zeolite type.**

Table 1

Optical properties of peroxide bleached pine TMP and eucalypt CCS pulp with various chelating agents

Pulp	Chelating system	Opacity %	Light Scattering cm²/g
TMP	No Chelation	90.5	526.0
	0.5% DTPA	89.6	514.9
	1.0% Z-A	90.3	533.1
	5.0% Z-A	90.6	563.5
	1% Z-A/0.5% Cit	90.4	523.6
	5% Z-A/0.5% Cit	91.0	549.8
CCS	No chelation	88.8	495.7
	0.5% DTPA	89.6	475.1
	1.0% Z-A	90.5	470.2
	5.0% Z-A	93.2	547.0
	1.0% Z-A/0.5% Cit	91.7	515.5
	5.0% Z-A/0.5% Cit	93.0	536.9

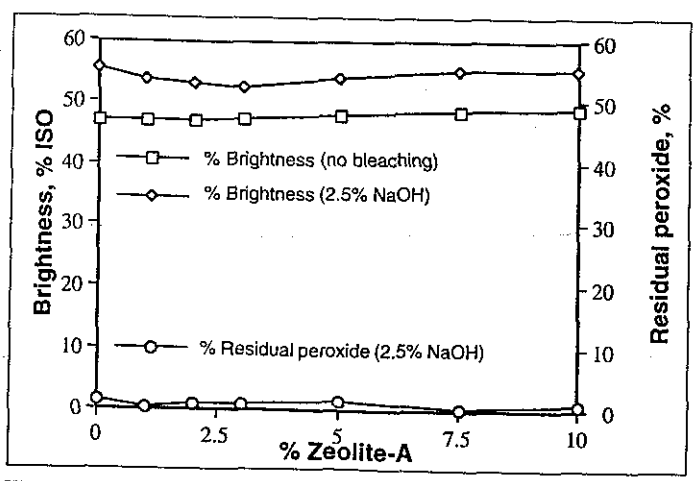

Fig. 7 **The effect on brightness and residual peroxide concentration of peroxide bleached eucalypt CCS by zeolite-A.**

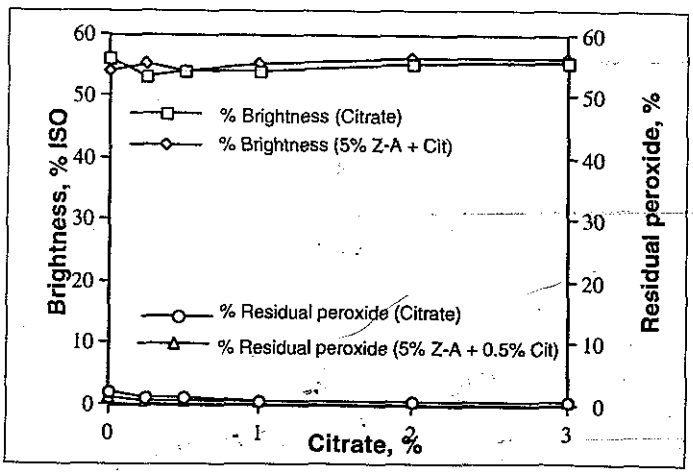

Fig. 8 **The effect on brightness and residual peroxide concentration of peroxide bleached eucalypt CCS by sodium citrate.**

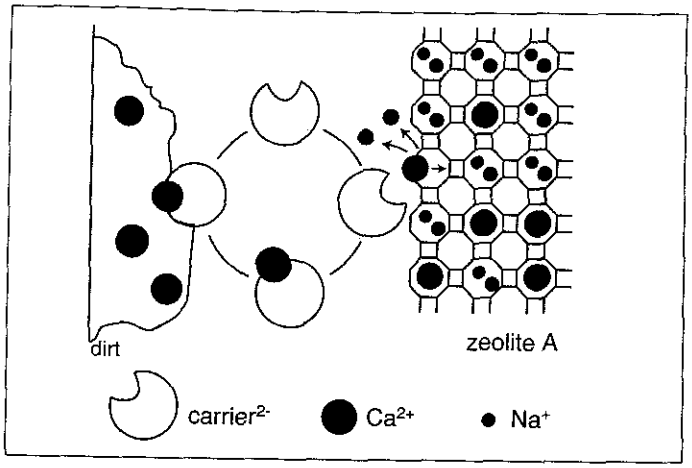

Fig. 9 The Carrier Effect (*15*).

the white colour of the zeolite to the pulp brightness.

Figure 8 shows that the addition of sodium citrate, with or without zeolite-A, has no significant effect on brightness and residual peroxide concentrations in peroxide bleaching of eucalypt CCS.

The poor performance of zeolite-A and sodium citrate alone or combined in chelating manganese and hence preventing peroxide decomposition, with consequently low or no brightness gains, is not entirely unexpected for eucalypt CCS pulp. In a previous study (*8*), zeolite-A and sodium citrate alone or combined in a model system containing no pulp failed to prevent manganese induced peroxide decomposition when alkali was added before the chelating agent. Addition of alkali is thought to convert Mn^{2+} to Mn^{4+} species or a conjugate system containing Mn^{3+}/Mn^{4+} which readily convert to Mn-O species(*12,13*) which are partially insoluble and seem unable to be exchanged into the zeolite. Therefore it would appear most likely that the alkali added to the eucalypt chips to help separate the fibres during the refining process is preventing zeolite-A and citrate from being viable chelating agents for eucalypt CCS. Furthermore, in the previous study (*8*), DTPA was not found to be affected by the form of manganese in reducing peroxide decomposition and has also been found to produce large brightness gains with significant residual peroxide concentrations over systems investigated in this study for the peroxide bleaching of eucalypt CCS.

Physical Handsheet Properties

Strength properties: The effects of different chelating systems (zeolite, zeolite-citrate and DTPA) on tearing resistance and tensile strength of pine TMP and bleached eucalypt CCS were examined. No significant differences were observed at the 95% confidence level between the mean values for the different chelating systems for tear and tensile indices. For TMP, the tear index varied between 8.6 and 9.4 $mN.m^2/g$ with an average 95% confidence interval of ±1.0 $mN.m^2/g$ while tensile index varied between 31 and 34.6 N.m/g with a 95% confidence interval of ±3.0 N.m/g. For CCS, the tear index varied between 4.1 and 4.9 $mN.m^2/g$ with an average 95% confidence interval of ±1.0 $mN.m^2/g$ while tensile index varied between 36 and 47 N.m/g with an average 95% confidence interval of ±5 N.m/g. Similar results have been reported in the literature (*14*).

Sheet roughness and porosity: The use of the various chelating systems in the peroxide bleaching of pine TMP did not have a significant effect at the 95% confidence level on roughness and porosity, despite some systems containing solid inorganic particles (zeolites). The roughness values varied between 5.3 and 5.7 µm with an average 85% confidence interval of ±1 while porosity varied between 471 and 713 mL/min with an average 95% confidence interval of ±300 mL/min.

There were no significant differences for bleached CCS handsheets with the different chelating systems. However the unchelated CCS had a higher porosity (1097 mL/min) than the chelated CCS. The roughness varied between 3.9 and 4.5 mm with a 95% confidence interval of ±0.5 while the porosity values for the chelated systems varied between 166 and 342 mL/min with a 95% confidence interval of ± 90 mL/min.

Optical properties: The effect of various chelating systems on opacity and light scattering coefficient of peroxide bleached pine TMP and bleached eucalypt CCS is shown in Table 1. Opacity decreased slightly, for both pulps, with addition of chelating systems containing none or only low amounts of zeolite. However with higher amounts of zeolite the level of opacity was roughly the same as that of the system containing no chelating agent.

Light scattering coefficient increased with addition of chelating agents, the most significant increases occurred with high levels of zeolite. Therefore it would seem most likely that the higher concentration of zeolite is having a small 'filler' effect by increasing the amount of air-surface interfaces to scatter light.

Proposed mechanism

A combined system of zeolite-A and sodium citrate performs better than zeolite alone and is comparable to DTPA in producing beneficial reduction in manganese induced peroxide decomposition, leading to brightness and residual peroxide improvements for peroxide bleached TMP. It is believed that zeolite-A acts as a cation exchange agent for Mn^{2+} ions that are bound at sites previously containing sodium ions. Since zeolites are solids they are therefore physically limited in the uptake of manganese ions from fibres. Sodium citrate on the other hand is believed to form soluble complexes with manganese and therefore can act as a transfer agent for manganese between fibres and zeolites in a similar manner known as the 'Carrier Effect' mechanism proposed for Ca^{2+} and Mg^{2+} ions in zeolite-based detergents (*15*) (Fig. 9).

The zeolite-citrate system is unable to prevent manganese induced decomposition if the zeolite-citrate is added under alkaline conditions. In the presence of alkali, manganese (Mn^{2+}) is oxidized to higher oxidation states (Mn^{3+} and Mn^{4+}) and forms complex Mn-O species. These species are most likely too large to be exchanged or trapped in the zeolite structure.

CONCLUSIONS

- For TMP, small amounts of sodium citrate and zeolite-A improved brightness and residual peroxide concentration to such an extent that it was nearly equivalent to DTPA alone.
- Sodium citrate alone required quantities of 3% or greater to obtain acceptable brightness improvements and residual peroxide concentration for bleached pine TMP.
- Zeolite-A was the best performing system of the three commercial zeolites

studied in terms of brightness improvement and residual peroxide concentrations for TMP.

- The optimum pretreatment time occurred within 1 hour for the zeolite containing systems with respect to both brightness and residual peroxide concentrations of bleached TMP.
- Zeolite and citrate were unable to prevent manganese induced peroxide decomposition in eucalypt CCS pulp.
- Tear and tensile indices, roughness and porosity of handsheets, were not significantly affected by the zeolite chelating systems for the TMP and CCS.
- Optical properties, opacity and light scattering coefficient, were improved particularly with chelating systems containing 5% zeolite-A.
- Sodium citrate seems to act as a transfer agent for manganese ions between pulp fibres and zeolites.
- Oxidized manganese species appear to be unable to complex and be trapped in the zeolite pore structure.

ACKNOWLEDGEMENTS

The authors thank Solvay-Interox Pty. Ltd. for their financial support for this project. We also thank Dr Bob Cox and Mr Paul Banham of Fletcher Challenge Paper, Boyer for their technical support.

REFERENCES

(*1*) Dence, C. W. and Reeve, D. W. – **Pulp Bleaching: Principles and Practice:** TAPPI Press (1996).

(*2*) Allison, R. W. – Peroxide bleaching of mechanical pulp from Pinus radiata, *Appita* **36**(5):362(1983).

(*3*) Singh, R. P. – **The bleaching of Pulp – 3rd edition** p.211 TAPPI Press (1979).

(*4*) Smith, P. K. and McDonough, T. J. – Transition metal ion catalysis of the reaction of a residual lignin related compound with alkaline hydrogen peroxide, *Svensk papperstid.* **88**(12):106 (1985).

(*5*) Galbacs, Z. M. and Csanyi, L. J. – Alkali induced decomposition of hydrogen peroxide, *J. Chem. Soc. Dalton. Trans*: 2353 (1983).

(*6*) Bambrick, D. R. – The effect of DTPA on reducing peroxide decomposition, *Tappi J.* **68**(6):96 (1985).

(*7*) Leonhardt, W., Suss, H. U. and Glaum, H. – German Patent DE 41 18 899 C1: (1992).

(*8*) Finnegan, D. J., Stack, K. R. and Dunn, L. A. – Peroxide bleaching with zeolites. Part 1: Peroxide decomposition, *Appita J.* **51**(3): 219 (1998).

(*9*) Bassett, J., Denney, R. C., Jeffrey and G. H., Mendham, J. – Vogel, **Textbook of quantitative inorganic analysis – fourth edition:** Longman (1978).

(*10*) Ginting, Y. – PhD Thesis, University of Tasmania, Australia (1997).

(*11*) Breck, D. W. – **Zeolite Molecular Sieves: structure, chemistry and uses:** Wiley and sons. (1974).

(*12*) Kanungo, S. B., Parida, K. M. and Sant, B. R. – Studies on manganese dioxide III. The kinetics and mechanism for the catalytic decomposition of hydrogen peroxide over different crystalline modifications of manganese dioxide, *Electrochim. Acta*, **26**(8):1157 (1981).

(*13*) Kanungo, S. B. – Physicochemical properties of manganese (IV) oxide and manganese (IV) oxide – copper (II) oxide and their relationship with the catalytic activity for hydrogen peroxide decomposition and carbon monoxide oxidation, *J. Catalysis* **58**(3):419 (1979).

(*14*) Rivard, J., Mohini, S., Leduc, C. and Daneult, C. – Role of zeolite in bleaching and its influence on fine retention, waste water quality and paper properties. ISWPC:4-1 (1997).

(*15*) **Technical Bulletin Pigments**, No 71 – Wessalith for Detergents, 4th edition, Degussa AG, Germany (1993).

Revised manuscript received for publication 22.7.98.

ERRATUM

APPLICATIONS OF THE SCANNING ELECTRON MICROSCOPE TO THE STUDY OF AUSTRALIAN NEWSPRINT MILLS PAPERS: PRODUCT EVOLUTION AND DEVELOPMENT

Christopher J. James, Anthony J. Rees and Michele K. Plummer

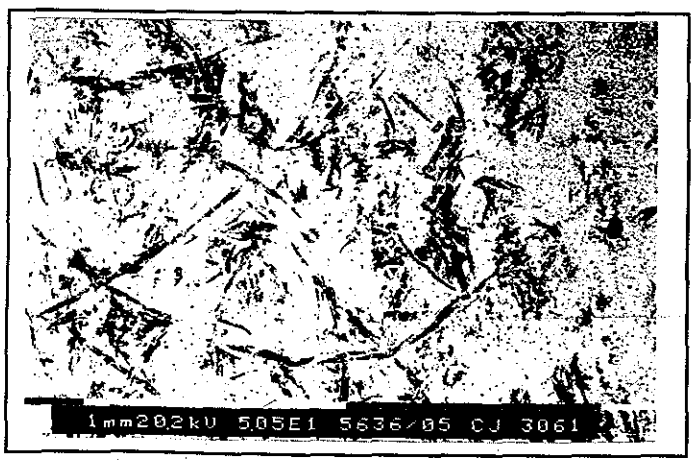

Plate 18